Vol. 13. Communication 273.

Bloomfield: Studies in Hevea Rubbers, Parts V and VI.

THE JOURNAL OF THE RUBBER RESEARCH INSTITUTE OF MALAYA

JANUARY 1951

Published by The Rubber Research Institute of Malaya
and
Printed by Charles Grenier & Son, Ltd., Kuala Lumpur, Malaya.

Edited by C. E. T. Mann on behalf of the Board of the Rubber Research Institute of Malaya.

Price 50 cents

EDITORIAL NOTE

Studies in Hevea Rubber

The investigations recorded in a series of papers published under the above general title have been undertaken at the Rubber Research Institute of Malaya by Dr. G. F. Bloomfield, of the British Rubber Producers' Research Association.

The work forms part of a joint programme of fundamental research undertaken by the British Rubber Producers' Research Association, and the Rubber Research Institute of Malaya.

Dr. Bloomfield came to Malaya in September 1948, and worked in the R.R.I. laboratories in Kuala Lumpur until January 1951. During the latter part of his stay, permanent members of the Institute's staff co-operated with him in the development of new lines of work arising from his fundamental studies.

The full series consists of six papers; Parts V and VI are contained in the present Communication.

Editor.

J.R.R.I.M. Communication 273.

STUDIES IN HEVEA RUBBER

Part V

Oxygenated and Low Molecular Fractions in Fresh Rubber.

By

George F. Bloomfield

The presence in rubber of oxygenated low molecular constituents with molecular weights (estimated from intrinsic viscosity) below 100,000 and oxygen contents in the range 0.3% to over 1%, indicated by previous work in Europe and in the East, has been confirmed, even when latex is collected and treated under conditions excluding access of air.

The oxygenated fractions are soft plastic rubbers which on hydrolysis undergo change into viscous gums of similar intrinsic viscosity to the corresponding unhydrolysed substances, but with reduced oxygen contents. Both the original oxygenated fractions and their hydrolysis products contain active hydrogen which, if present in hydroxyl or carboxyl groups, corresponds to an appreciable proportion of the oxygen contents.

The precise analytical work of Midgley, Henne, Shepard and Renoll(1) showed that rubber hydrocarbon purified by fractional precipitation in the absence of air contained a small proportion of combined oxygen (0.04%), half of which appeared to be hydroxylic. Later, Roberts(2) isolated from fresh rubber in the East a fraction designated " caoutchol " containing two or three units per cent of oxygen which appeared to be present in the form of an ester of a lightly hydroxylated polyprene of relatively low molecular weight. No precautions were, however, taken to guard against autoxidation, and Kraay and Altman(3) showed that increased exposure to air in Roberts' separative procedure substantially increased the proportion of material isolated in the " caoutchol " fraction, and, furthermore, when the separation was conducted in an atmosphere of nitrogen the amount of the " caoutchol " fraction was reduced somewhat, although it did not become zero. Kraay and Altman did not, however, state whether their material was chemically, or even physically, identical with that of Roberts.

During some experiments on fractionation of rubber by a dissolution technique the present author with Dr. E. H. Farmer(4) isolated oxygen-containing fractions

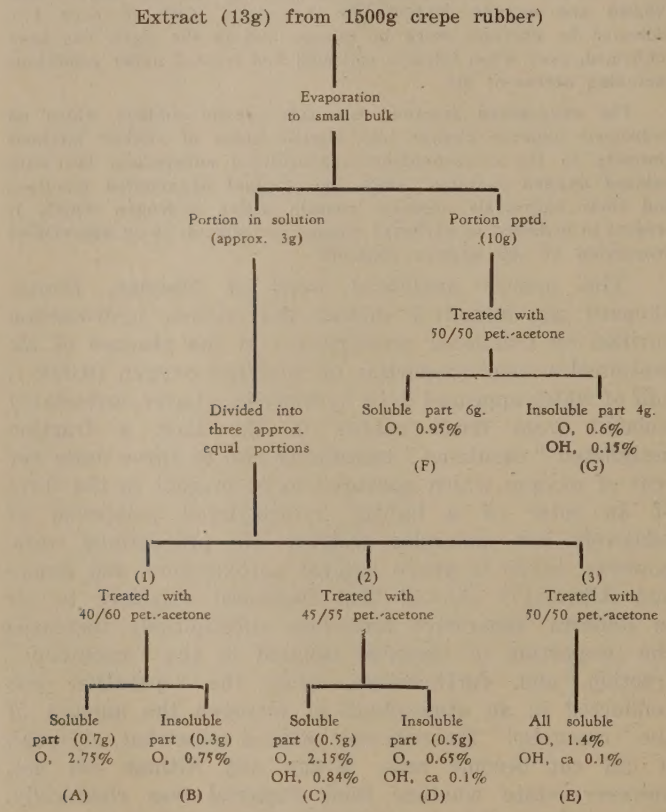
from crepe rubber, from dried latex film, and from rubber latex shipped to England in sealed containers after preservation with sodium pentachlorophenate in the East.

Properties of oxygenated low-molecular fractions extracted in England

Table I shows a separative procedure applied to a low-molecular product originally extracted from 1500g. of acetone-extracted crepe rubber between the limits of 48/52 to 52/48 petroleum (40-60°)—acetone in the apparatus of Michael(4).

Table I

Sub-fractionation of a low-molecular fraction of crepe rubber.


Extract (13g) from 1500g crepe rubber)
Evaporation to small bulk
Portion in solution (approx. 3g)
Portion pptd. (10g)
Treated with 50/50 pet.-acetone
Soluble part 6g. O, 0.95%
(F)
Insoluble part 4g. O, 0.6% OH, 0.15%
(G)
Divided into three approx. equal portions
(1) Treated with 40/60 pet.-acetone
(2) Treated with 45/55 pet.-acetone
(3) Treated with 50/50 pet.-acetone
Soluble part (0.7g) O, 2.75%
(A)
Insoluble part (0.3g) O, 0.75%
(B)
Soluble part (0.5g) O, 2.15% OH, 0.84%
(C)
Insoluble part (0.5g) O, 0.65% OH, ca 0.1%
(D)
All soluble O, 1.4% OH, ca 0.1%
(E)

The oxygen contents in the above table were differences between 100% and the totals of C, H (ash contents being generally small).

Hydroxyl contents were determined by the method of Bolland(5).

This sub-fractionation thus yielded components progressively lower in oxygen content when the original extract was allowed to diffuse into solvent mixtures progressively richer in petroleum. The combined oxygen appeared to be present in these fractions partly in non-hydroxylic form, suggesting that the fractions might be chemically similar to "caoutchol" even though physically they were quite different, being soft, sticky plastic materials with little or no rubberlike elasticity. The chemical similarity to caoutchol suggested the desirability of applying a hydrolytic treatment, and small samples were accordingly sealed under vacuum in tubes containing (per g. of sample), benzene (20 ml.) and 0.2N alcoholic potassium hydroxide (2 ml.), after degassing the solvents, and heated for 4 hours at 60°. The contents of the tubes were then centrifuged to remove a precipitated gelatinous substance and the clarified solutions were greatly diluted with ether and washed free from alkali. (Larger amounts of material were hydrolysed under reflux in a stream of nitrogen at the boiling point of the solvent mixture). Soluble neutral products of hydrolysis isolated from these solutions ranged from cold-flowing yellow viscous gums with no rubberlike properties to soft sticky rubbers, according to the oxygen contents of the fractions before hydrolysis (Table II). The insoluble matter separated by centrifuging was also insoluble in a wide range of solvents, but when treated with acetic acid in a benzene-alcohol medium its acidic constituent was liberated and remained in solution, enabling inorganic salts to be removed by washing. A sample of this material, isolated in England from a sample of "caoutchol" prepared in Malaya in 1941(6), and representing 11% of the original material, was a crumb-like acidic substance of considerable molecular weight which could only be brought into solution in mixtures of benzene and alcohol (Found: C, 84.8; H, 11.9; iodine value 180; equiv. *ca.* 1000; $[\eta]$ 0.24 in benzene + 15% methanol). The composition of a silver salt (Found: Ag, 9.5%) prepared from the sodium salt of the acidic material was in agreement with the observed oxygen-content (calc., 3.1%) and equivalent (calc., 1020) of the free acid. (It follows that the acidic component must have been of considerable molecular magnitude since the acid was obtained in 11% yield, yet the hydroxyl content (0.2%) calculated from the active hydrogen in the corresponding neutral component was so small as to give but few points of attachment of acidic material).

The active hydrogen contents of the samples before and after hydrolysis indicated that the hydroxyl content of the unhydrolysed material must have been present in the acidic constituent, possibly in free carboxyl groups (a small "acid value" of rubber has been reported(7)). With this assumption the above data are consistent with the hydrolytic fission of an ester group involving a hydroxyl group in the polyisoprene chain and a high molecular carboxylic acid.

Table II

Hydrolysis products of some oxygenated fractions examined in England.

Fraction	Oxygen and active hydrogen contents			
	Before hydrolysis		After hydrolysis	
	0%	active H%	0%	active H%
A, table I ..	2.75	.017	0.7	.017
C, „ „ ..	2.15	.049	1.0	.049
E, „ „ ..	1.4	.006	0.9	.012
G, „ „ ..	0.6	.009	0.3	.012
"Caoutchol" ..	2.5	.028	0.7	.013

Properties of oxygenated low molecular fractions extracted in Malaya

Owing to the difficulty of maintaining stocks of petroleum in a peroxide free condition in the tropics, the benzene-alcohol azeotrope of composition 65.2% benzene by volume and b.p. 68.24° has been used for extraction of low molecular fractions in Malaya. The mixture becomes a solvent for rubber at temperatures above 50°, but at 20° it extracts only non-rubber constituents, consequently, a progressive increase of extraction temperature between these limits provides a convenient method of extracting fractions of progressively increasing molecular weight.

The extraction apparatus used in Malaya was similar to that of Michael(4), but it was found more convenient to replace the glass bottle by an aluminium container in which the rubber could be distributed over a series of baffle-plates, so rendering extraction more efficient by preventing the rubber from massing together at the bottom of the apparatus. For temperature control the aluminium container was placed in a thermostat. In order to ensure in at least one instance that the rubber sample was as representative as possible of that leaving the tree, latex was collected in a bottle, in which an atmosphere of nitrogen was maintained, while nitrogen was also blown over the tapping cut which was bridged by paper secured to the tree with adhesive tape. Latices were coagulated by pouring into acetone in a shallow tray and the resulting sheets were consolidated, rolled thin, extracted with acetone in the aluminium container of the extraction apparatus and finally freed from acetone by evacuation into a high-vacuum system while being contained in a large desiccator. (Acetone extraction was omitted in the first sample examined, and the fractions were themselves individually acetone-extracted).

Table III shows the properties of some low-molecular fractions isolated in Malaya, including sub-fractions obtained by benzene-methanol fractionation of some of the primary fractions. Most of the fractions contained more oxygen* than could be accounted for by their ash-contents. (The oxygen-contents were determined by Dr. W. T. Chambers using a modification(8) of the Unterzaucher method).

For an absolute determination of the oxygen content it was clearly most desirable to obtain relatively ash free fractions comparable to those isolated from crepe rubber in England, but washing and machining of the rubber prepared as above was not permissible owing to the risk of oxidative degradation and there were strong practical objections to purifying the latex since treatment with ammonia, necessary for preservation of the latex during purification, is known to reduce the oxygen-content and alter the character of low molecular fractions in a manner similar to that brought about by hydrolysis(4). An alternative method of soap-displacement purification at pH 7-8 using latex preserved with sodium pentachlorphenate and buffered with phosphates gave fractions with even larger ash contents than unpurified (but acetone-extracted) rubber, doubtless due to formation of calcium and magnesium soaps which were soluble in the benzene-alcohol azeotrope but were insoluble in acetone.

* The fractions were shown to be free from peroxidic oxygen by the method of Bolland(9). No peroxidic oxygen has been observed in fresh latex, and after conversion into smoked sheet the peroxidic oxygen content does not exceed 30 parts per million.

Table III

Low-molecular fractions of fresh Hevea rubber.

Rubber	Tem. of extraction	% fraction in rubber	Analysis					$[\eta]$
			C%	H%	O%	N%	ash %	
Rubber not acetone-extracted ..		.04	—	—	—	—	—	.18
		.06	84.0	11.85	1.9	.07	2.45	.24
		.10	84.5	11.85	2.2	.05	1.1	.31
	30° ..	.17	82.8	11.7	2.7	.07	2.45	.40
		.18	86.5	11.9	1.1	—	0.9	.61
		.34	85.7	11.8	0.65	—	1.45	.69
		.44	86.1	11.7	1.1	—	0.9	.70
		.52	85.7	11.9	1.2	—	0.9	.72
		.50	87.1	11.8	0.6	—	0.5	.96
	37° ..	.19	86.4	11.65	1.1	—	0.85	1.10
	42° ..	.38	86.65	11.8	0.8	—	0.7	1.7
	48° ..	.85	87.4	11.8	0.5	—	0.1	2.8
Latex of tree 3, collected under nitrogen ..	35° ..	1.5	87.3	11.85	0.47	0.05	0.15	.52
		2.2	87.4	11.8	0.40	—	0.15	.69
	40° ..	1.8	87.4	11.9	0.30	—	nil	1.07
Latex of soft trees (Group A)	30° ..	0.25	74.0	10.7	9.0	—	7.0	.14
		3.4	87.1	11.8	0.9	—	0.4	.60
Latex of soft trees (Group A)		0.2	—	—	—	—	—	—
	35° ..	1.0	86.4	11.8	1.0	0.06	0.85	.41
		1.1	87.8	11.9	0.46	—	0.15	.82
		0.4	87.5	11.9	0.47	—	0.25	1.25
	40° ..	0.9	87.7	11.8	0.35	—	0.2	1.10
Latex of hard trees (Group G)		0.35	73.0	10.55	8.95	—	7.4	0.19
	35° ..	1.75	86.9	11.9	0.8	0.04	0.8	0.67
		1.25	87.6	11.75	0.53	—	0.3	0.86
	40° ..	1.2	87.4	11.8	0.25	—	0.1	1.26

After hydrolysis the oxygenated fractions exhibited the same general characteristics as those examined in England. The very pronounced change in the physical nature of the material—from soft plastic rubber to viscous gum—was not accompanied by any marked change in intrinsic viscosity (Table IV).

Table IV

Hydrolysis of three oxygenated fractions isolated in Malaya.

	$[\eta]$	Analysis				
		C	H	O	ash	active H
Before hydrolysis ..	.60	87.1	11.8	0.9	0.4	.0153
After „ * ..	.47	87.55	11.9	0.4	0.2	.0124
Before hydrolysis ..	.69	87.4	11.8	0.4	0.15	.006
After „ * ..	.59	87.6	11.9	0.3	0.2	.006
Before hydrolysis ..	.41	86.4	11.8	1.1	0.85	.0159
After „ * ..	.39	87.7	11.85	0.42	0.1	.0147

* Neutral products of hydrolysis.

The extraction method, while convenient for obtaining relatively large quantities of low molecular material, does not quantitatively extract any given intrinsic viscosity range owing to consolidation of the rubber on the baffle-plates in the mixed solvent. It is not therefore possible with the diffusion method to make reliable comparisons of the relative amounts of any particular fraction in different rubbers.

Isolation of low-molecular fractions by precipitation

In the fractionations described in Part III, small proportions of low molecular fractions in a large volume of solvent remained after precipitation of the bulk of the rubber, and the isolation of these fractions involved considerable risk of degradation. When the major part of the rubber content was precipitated from fairly concentrated solutions the task of isolating the remaining low-molecular material was simplified and it has been demonstrated in Part III that a typical oxygenated low-

molecular fraction could be isolated without degradation by this procedure. This confirmed that the character of fractions isolated by the extraction (diffusion) method was not changed by heating the solution of the extract at the boiling point of the solvent mixture.

Two low molecular fractions were also isolated by means of the carbon tetrachloride-acetone mixtures used by Roberts(2). These were again no different from the fractions obtained by extraction; the soft tree group (A) yielded 9.1% of a soft plastic rubber with intrinsic viscosity 0.7 (Found: C, 87.2; H, 11.9; ash 0.1; O, 0.65%) and the hard tree group (G) yielded 2.2% of a similar product with intrinsic viscosity 0.77 (Found: C, 85.8; H, 11.65; ash 0.6; O, 1.6%). The difference in yield is probably significant.

Summary and Conclusions

Fresh Hevea latex, even when collected under conditions excluding access of air as far as possible, yields rubbers from which small proportions of fractions of low molecular weight can be isolated by either diffusion or precipitation methods. These fractions contain combined oxygen in excess of that which can be accounted for in combination with mineral-containing impurities the presence of which is revealed by an appreciable ash content when the fractions are ignited. The oxygen content decreases as the intrinsic viscosity of the fractions increases, and when the intrinsic viscosity is greater than unity (estimated molecular weight above 100,000) the amount of combined oxygen is 0.3% or less. On the assumption that the mineral content is mainly due to metallic salts of carboxylic acids, the oxygen combined with the hydrocarbon in fractions of intrinsic viscosity 0.75 (estimated molecular weight *ca.* 50,000) is *ca.* 0.5% rising to a little over 1% in fractions with intrinsic viscosity below 0.5 (estimated molecular weight below 30,000).

The oxygenated fractions contain active hydrogen corresponding to 30-50% of the combined oxygen if the active hydrogen is present in hydroxyl groups, and to most if not all of the combined oxygen if it is present in carboxyl groups.

Hydrolysis of oxygenated fractions yields as major products neutral viscous gums which have intrinsic viscosities little different from those of the parent

substances. The oxygen content is reduced on hydrolysis but the active hydrogen content is not significantly changed. In the neutral products of hydrolysis the active hydrogen is believed to be present in hydroxyl groups corresponding to points of attachment of an acidic component of considerable molecular magnitude which is also liberated on hydrolysis.

Preciptitation methods are of more promise than diffusion methods for quantitative separation of low molecular fractions, although the latter methods are of advantage when a considerable amount of low molecular material is required.

It is further proposed to study the variation in the proportion of oxygenated components between trees, and also the effect of processing and storage on the proportion of oxygenated material present.

Acknowledgments

The author acknowledges the assistance of Dr. W. T. Chambers (B.R.P.R.A.) for the microanalyses recorded in this paper, which forms part of the programme of fundamental research undertaken by the Boards of the British Rubber Producers' Research Association and the Rubber Research Institute of Malaya.

The author particularly desires to record his appreciation of the co-operation of Mr. M. W. Philpott, Head of the Chemical Division of the Rubber Research Institute.

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STUDIES IN HEVEA RUBBER

Part VI

Characteristics of Rubber in Latex of Untapped Trees and in Branches of Trees in Regular Tapping.

By

George F. Bloomfield

The discovery that the latex in some untapped trees, and in the branches of some trees in regular tapping, contains a high proportion of microgel enables important conclusions to be drawn as to the area of bark affected by tapping, since, when an untapped tree is brought into production, the microgel latex contained in a considerable area of the tree is replaced by normal latex. Certain clonal species, notably P.B.186, do not contain very much microgel latex even when old untapped trees are examined.

Microgel latex has certain novel characteristics. Its rubber content can be brought into solution in benzene to give solutions of very low inherent viscosity, but only small osmotic pressure. Rubbers obtained from microgel latex are not of low molecular weight and are in fact very hard.

When two tapping cuts are opened on a single tree, the upper cut at first contains more microgel latex than the lower cut, and yields rubber which is correspondingly harder.

Experience in rubber-producing territories has established that severe increases in the intensity of tapping of *Hevea brasiliensis* give softer rubbers, with depletion of the rubber content of the tapped latex. No information is, however, available to show whether there is any corresponding change in plasticity of rubber when trees are brought into tapping for the first time or after long periods of resting, i.e. an increase of tapping intensity from zero to normal, although it is known that the rubber content of the tapped latex(1) falls progressively from an initially high value (frequently >50%) to an equilibrium value determined by the tapping system employed.

Since *Hevea brasiliensis* possesses a latex system of inter-communicating vessels, it is not surprising that withdrawal of latex at the tapping cut affects the concentration of latex over a considerable area of the bark of the tree(2 4). Estimates of the area of bark affected vary considerably, possibly depending on the tree, but a reduction in the rubber content of the latex at sampling points as remote as thirty feet above the tapping cut has

been observed after only three tappings of a newly opened tree.

When the technique of taking samples of latex into benzene (Part I) was applied to trees which had not been tapped for 8 years, as well as to some 20 years old trees which had not previously been tapped, it was immediately apparent that the latex from trees representative of several clones had different solubility characteristics compared with normal latex since, on shaking, the rubber phase first disintegrated into small, swollen particles which required considerable further shaking to bring them into solution. After dehydration the solution remained hazy and had quite low inherent viscosity which increased slightly with concentration (Table I and Fig. I); when poured from one vessel to another the solution left an insoluble rubber film on the walls of the container. In the group of trees examined, one particular clone, P.B.186, gave a normal latex, i.e. latex with solubility characteristics as described in Part I, passing into solution after a few minutes shaking to give intrinsic viscosity in the range 4-7.

Table I

Inherent viscosity of rubber in untapped and in long rested trees.

Clonal type	Inherent viscosities [a] of latex solution from 28 different trees					
Av. 49 ..	1.3	3.0	1.0	1.0	0.8	0.6
Av. 152 ..	2.2	2.8	0.8	1.4	—	—
Tj. 1 ..	1.0	1.0	1.4	0.9	0.5[b]	—
Rub. 393 ..	2.0	1.1	1.6	3.6[c]	—	—
P.B. 186[d] ..	6.2	5.6	5.4	4.4	4.5	5.0
P.B. 186[b] ..	4.4	3.2	—	—	—	—
B. 84 ..	1.1	—	—	—	—	—

Notes: (a) Inherent viscosities were determined at concentrations ca 0.1g/100 ml.

(b) These trees were 20 years old and had not previously been tapped.

(c) This tree had been badly wind-damaged.

(d) Inherent viscosities of P.B.186 samples were independent of concentration.

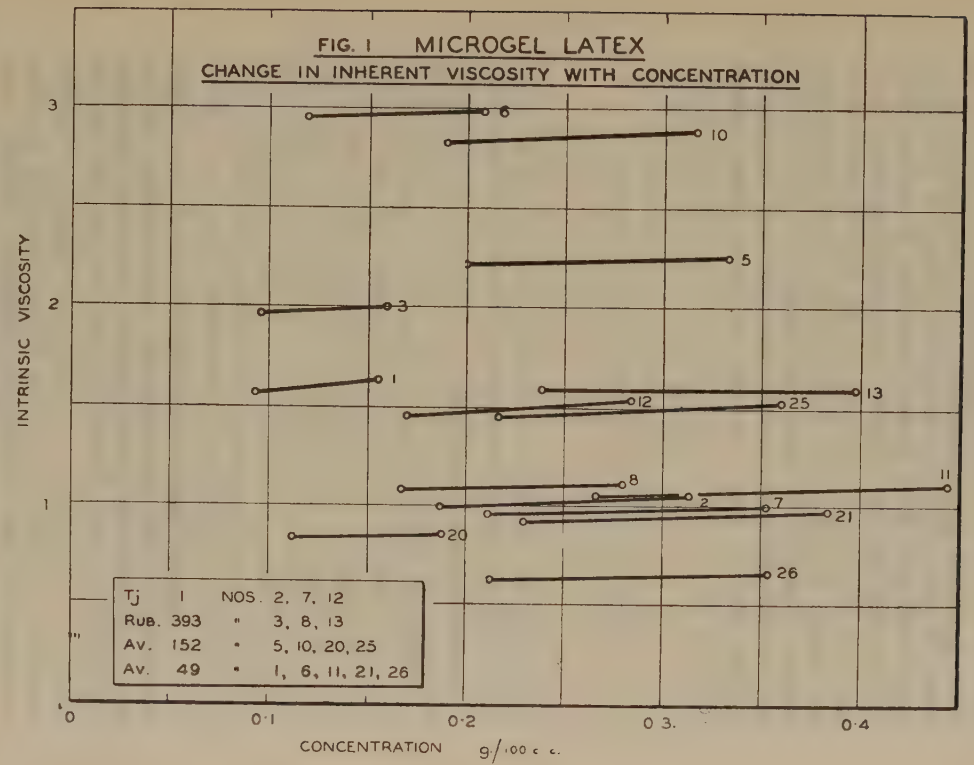
FIG. 1 MICROGEL LATEX
CHANGE IN INHERENT VISCOSITY WITH CONCENTRATION
INTRINSIC VISCOSITY
CONCENTRATION g/100 c.c.
3
2
1
0
0·1
0·2
0 3.
0·4
6
10
5
3
1
13
12
25
8
11
2
7
21
20
26
Tj 1 NOS. 2, 7, 12
Rub. 393 " 3, 8, 13
Av. 152 " 5, 10, 20, 25
Av. 49 " 1, 6, 11, 21, 26

When the rubber was precipitated from benzene solutions of latices of the above abnormal type and dried in vacuo, it could not be redissolved in either benzene or benzene-methanol. Precipitation of the rubber was practically quantitative, 88-92% of the total solids (estimated by evaporation of a portion of the solution) being found in the precipitate. The data presented in Table VII show that the non-rubber content of latex from long-rested trees is no greater than that of normal latex, consequently the low intrinsic viscosities observed could not have been due to an abnormally high proportion of non-rubber substances in these latices. The precipitated rubbers (Table II) were in fact rather less contaminated with nitrogenous and mineral impurities than precipitated rubbers derived from solutions of more normal latices (cf. Part I).

Table II

Characteristics of rubbers precipitated from solutions of latices of Av.49 and Tj.1 long-rested trees.

	Av. 49	Tj. 1
Inherent viscosity of latex solution	0.76	0.95
Proportion of total solids pptd. ..	91%	89%
Analysis of pptd. rubber: C ..	86.6	86.25
-do- H ..	11.7	11.6
-do- N ..	0.44	0.44
-do- Ash ..	0.08	0.25
-do- O* ..	1.16	1.15

* Directly determined.

The almost quantitative preciptation of the rubber from solution and the insolubility and toughness of the precipitated rubbers proved beyond doubt that the above rubbers were not of low molecular weight (cf. characteristics of fractions of comparable inherent viscosity described in Part V). Even before removing residual solvent from the precipitated rubbers, difficulty was experienced in redissolving them completely and at best, only "specky" solutions could be obtained, containing discreet swollen gel particles. The solvent-free precipitated rubbers were only swollen to a limited extent in benzene, thus resembling lightly vulcanised rubber, and estimates of

the degree of swelling were obtained by visual measurements or rapid weighing of the swollen samples. These are shown in Table III in which Qm is the swelling index expressing the volume of benzene absorbed per unit volume of rubber.

Table III

Swelling index of rubbers from long-rested trees.

Preparation of samples	Clonal type	L.S.V.	Qm.
Pptd. from solution ..	R.R.I. 514	2.1	29
„ „ „ ..	R.R.I. 513	1.9	28
„ „ „ ..	Av. 49	1.0	20
Ace-tone-extracted coagulum from purified latex ..	same tree	—	20
Pptd. from solution ..	Av. 49	0.8	11
„ „ „ ..	Tj. 1	0.5	9

Vacuum-dried films of the abnormal types of latex could be brought into solution by violently shaking with benzene within a few minutes of their preparation. The inherent viscosity (1.1) of one of these solutions was identical with that of the solution of the corresponding latex. Vacuum-dried coagula were mainly insoluble.

All the characteristics of the above abnormal latices were consistent with the conception of a cross-linked structure confined to the individual latex particles, and such a latex has accordingly been designated "microgel latex"(5) (cf. Part II). An alternative term "primary rubber", which has been used to differentiate between the rubber in an untapped tree and that synthesised subsequent to withdrawal of this rubber by bringing the tree into tapping, is too general in its implication; it does not differentiate between the normal latex in untapped P.B.186 and microgel latex, both of which contain "primary" rubbers.

Soluble components of rubber isolated from microgel latex

Although the vacuum dried coagula were substantially insoluble in a variety of solvents, relatively small amounts of soluble components were extractable when a finely-

shredded acetone-extracted rubber was immersed in solvents for several days in an atmosphere of nitrogen (Table IV). The soluble components had intrinsic viscosities considerably higher than the inherent viscosity of the original latex in solution: another point of interest is that fractionation by benzene-methanol of one of these soluble components (Table V) yielded a low-molecular fraction, characterised by its softness and ready solubility, with a rather higher oxygen content than fractions of corresponding intrinsic viscosity isolated from normal latex (cf. Part V).

Table IV

Soluble components of rubber from microgel latex.
(Ar. 49 + Tj. 1 mixture L.S.V. 1.3)

Solvent	Successive extraction†	% Rubber extracted	$[\eta]$ in benzene of soluble component
Benzene	1	1.5	3.26
	2	12	3.68
	3	4	3.38
Benzene + 15% methanol	1	11.4	3.03
	2	5.2	3.50
	3	2.1	—
	4	1.2	—
Benzene + 20% methanol	1	3*	0.69
	2	5	1.63

† Extractions for successive 3-day periods.

* This would be reported as "97% gel" in the R.R.I. method of gel determination. (see Table III in Part IV).

Table V

Sub-fractionation of soluble component extracted by benzene + 15% methanol.

Fraction	% in soluble component	$[\eta]$	Analysis				
			C	H	Ash	N	O
1	70	3.7	87.7	11.8	nil	nil	0.25
2	30	1.56	85.3	11.7	0.34	0.05	2.0

Osmotic Pressure of a Solution of Microgel Latex

The conception of microgel latex as a system of cross-linked particles was supported by attempts to measure the osmotic pressure of a dehydrated solution of

a microgel latex with inherent viscosity 0.62. No measurable osmotic pressure was developed by solutions of concentration less than 0.5% by weight, and at the highest concentration examined (0.89%) the osmotic pressure was only 0.111 cm., indicative of an enormous molecular weight.

Inherent Viscosity of Microgel Latex in Benzene + 15% Methanol

The restriction imposed on uncoiling of polymer molecules when passing from a poor solvent to a good one, is indicative of cross-linking. This results in a lowered ratio of the intrinsic viscosities in benzene and in benzene-methanol (Part III). Solutions of the rubber phase of several microgel latices gave a considerably lower ratio of intrinsic viscosities (1.5 to 1.8) than solutions of normal rubbers (cf. Table VII of Part III).

Plasticity of Rubber From Microgel Latex

From the considerations under discussion in Part IV, it follows that rubber of such high gel content as that obtained from microgel latex should be very hard. This is confirmed by the data in Table VI.

Table VI

Williams plasticity (D_{10}) of rubbers from microgel latex.

Treatment of latex	Av. 49 L.S.V. 1.0	Bulk Latex L.S.V. 2.1	
	D_{10} m.m.	D_{10} m.m.	Rec. m.m.
Coagulated, vacuum-dried ..	6.62	5.68	8.62
-do- + acetone extraction	7.77	7.49	12.5
Multi-creamed, coagulated, vacuum-dried	—	6.49	10.77
-do- + acetone extraction	—	6.52	12.07
Purified,* coagulated, vacuum-dried	6.52	6.32	10.84
-do- + acetone extraction	8.82	7.52	13.84

* Purified by soap-displacement and multi-creaming, (^{6})N-contents 0.04% and 0.06% respectively.

Table VII

Changes in latex on bringing into tapping two trees which had been rested for 18 months.

Tapping No.	R.R.I. 513					R.R.I. 514				
	Yield ml.	T.S. %	D.R.C. %	L.S.V.	D_{10} m.m.	Yield ml.	T.S. %	D.R.C. %	L.S.V.	D_{10} m.m.
1 ..	15	58.9	—	1.6	—	12	55.6	—	2.1	—
2 ..	36	—	50.7	1.7	6.01	30	50.1	—	2.1	6.10
3 ..	77	51.4	48.4	1.9	5.36	48	51.8	49.0	2.2	5.04
5 ..	98	48.0	44.1	3.7	3.21	75	50.0	47.0	3.4	4.62
7 ..	124	46.1	42.9	3.2	3.61	100	44.4	41.5	2.75	4.15
9 ..	120	44.5	41.3	3.5	3.53	98	44.0	41.0	2.9	4.36
12 ..	101	43.9	40.7	3.4	3.37	83	44.2	41.0	3.1	4.26
15 ..	23	48.8	45.7	4.0	2.89	18	47.6	43.8	3.7	3.71
21 ..	48	48.9	45.5	3.9	—	39	47.2	43.6	4.1	—

Notes: (1) Plasticity determinations on vacuum-dried coagula.

(2) *Dried* rubbers were not completely soluble until after the 10th tapping.

(3) Refoliation affected yields after the 13th tapping.

Now since the rubber-content of latex in an untapped tree gives solutions of very low inherent viscosity and also gives a very hard rubber, it follows that considerable changes must occur in the characteristics of latex and of the rubber derived from it when untapped trees are brought into regular tapping. Table VII, which records observations on two individual trees which had been out of tapping for eighteen months, and Table VIII which gives similar data for bulk latex from previously untapped trees (illegitimate seedlings, about 12 years old, from high-yielding mother trees), shows that the change from microgel to normal latex is practically complete in ten consecutive half-spiral alternate daily tappings. During this period the inherent viscosity of solutions of the latex increases while the rubber becomes progressively softer, which emphasises the point made in Part IV that there is no general correlation of intrinsic viscosity with plasticity.

Table VIII

Changes in bulked latex on bringing 114 untapped trees into production.

Tapping No.	Yield litres	L.S.V.	Vacuum-dried coagula		Smoked sheet			
			D_{10} m.m.	Rec.	D_{10} m.m.	Rec.	Mooney	% Gel*
1	1.5	2.1	5.68	8.62	5.45	9.37	120	85
2	2.0	3.2	5.40	8.46	4.56	6.48	98	84
3	2.7	3.8	4.78	7.22	3.83	5.09	88	82
4	2.8	4.3	4.95	7.51	3.78	4.80	82	82
5	3.5	4.5	4.35	6.12	3.62	4.30	77	80
6	5.7	4.6	4.31	5.25	3.42	4.07	74	77
8	5.7	4.3	3.84	4.98	3.54	4.12	67	74
9	4.5	4.2	3.92	5.08	3.51	4.13	72	72
12	8.5	4.1	3.50	4.48	3.26	3.66	58	72
25	10.2	4.1	—	—	3.28	3.76	62	66

* Gel. content was determined by the R.R.I. method (see Part IV).

Characteristics of Latex in Different Parts of a Tree

Examination of trees which had not been tapped for 8 years showed a fairly uniform distribution of microgel latex throughout the tree (Table IX) when samples were taken from small incisions in the bark.

Table IX

Microgel latex distribution in long-rested trees.

Tree	L.S.V. at height above ground:—			
	4 ft.	10 ft.	20 ft.	30 ft.
Av. 49 ..	.82	.36	.39	.44
Tj 1 ..	.83	.75	.41	.51

Determination of the area in which microgel latex is subsequently replaced by normal latex might, therefore, reveal the area of a tree affected by tapping. From a field of mixed illegitimate seedlings there were selected four high-yielding trees giving soft rubber, four high yielding trees giving hard rubber, four low-yielding trees giving soft rubber and four low-yielding trees giving hard rubber, as well as a representative selection of the trees studied in the previous parts of this series of papers. Table X shows that microgel latex is found in some parts of trees which have been in regular tapping for ten or more years, and also reveals a tendency for high-yielding trees to drain latex from a much greater area of the tree than low-yielding trees. Some low yielding trees behave similarly to the high yielders; these may, of course, be trees incapable of yielding much latex so that the small yield obtained may also be drawn from a considerable area.

There is no correlation between plasticity and area of drainage of microgel latex, and consequently, no indication that hardness and high gel content of some rubbers might be due to continual infiltration of microgel latex from more remote parts of the tree.

In the above survey three trees were included from a P.B.186 x Tj.1 clonal cross. Although rested for only a comparatively short time they seem to indicate that the capability of P.B.186 for synthesis of normal latex rather than microgel latex is inherited by the clonal cross since untapped Tj.1 latex usually shows typical microgel characteristics.

It is proposed shortly to determine the rubber content of latex in different parts of a tree by Ferrand's drop technique(4) since it follows that, if microgel latex persists in the upper regions of a tree, there can be no *rapid* transport of rubber from these parts to the tapping cut.

Consequently no loss of rubber resulting from tapping should be observed in parts of a tree where microgel latex is still present. Unfortunately the only data available(2) on the dilution effect in various parts of a tree do not differentiate between regions containing microgel and normal latex.

Table X

Characteristics of latex in different parts of trees.

Tree No. or type	Description	L.S.V. at height above ground		
		Tapping cut	20 ft.	30 ft.
	20 year old-trees in regular tapping:—			
1 ..	High yield, soft rubber	4.0	4.8	—
2 ..	„ „ hard „	5.0	2.4	1.5
14 ..	Medium „ soft „ *	5.6	0.8	0.5
15 ..	High „ hard „	5.2	3.9	4.5
17 ..	Medium „ hard „	7.1	1.5	0.35
1- 1 ..	High „ soft „	5.2	5.7	5.5
23-13 ..	„ „ „ „	5.3	6.0	4.1
41- 5 ..	„ „ „ „	5.7	3.8	2.5
52- 7 ..	„ „ „ „	6.7	3.1	1.3
10-16 ..	„ „ hard „	6.4	4.8	3.1
11- 1 ..	„ „ „ „	5.9	4.7	3.7
10-19 ..	„ „ „ „	6.4	5.1	2.4
52-12 ..	„ „ „ „	6.8	6.8	5.0
3- 7 ..	Low „ soft „	5.8	3.7	2.0
6- 4 ..	„ „ „ „	4.9	4.2	4.5
6-17 ..	„ „ „ „	6.5	1.9	2.3
6-22 ..	„ „ „ „	6.6	0.68	0.59
14- 1 ..	„ „ hard „	6.9	1.3	0.7
22- 3 ..	„ „ „ „	7.6	1.0	0.7
31- 3 ..	„ „ „ „	7.0	5.3	1.6
8- 2 ..	„ „ „ „	7.8	1.3	0.9
P.B.186 ..	High „ „ „	5.7	5.3	2.2
	Tree not previously tapped	(trunk)		
P.B.186 ..		3.2	2.2	1.7
	Trees rested two years			
(a) ..	Clonal cross P.B.186 x Tj.1	6.4	6.0	3.7
(b) ..	„ „ „ „	6.7	6.4	6.3
(c) ..	„ „ „ „	6.8	6.4	6.0

* In this tree samples taken 10 ft. above tapping cut and from a root had L.S.V. 3.8 and 5.2 respectively.

Tapping of Isolated Islands of Bark

Bobillioff(7) and Frey-Wyssling(8) reported that bark islands could continue to yield rubber over considerable periods of time. Recent experiments on two trees, one of which (Tj.1) had not been previously tapped, did not confirm these observations when islands approximately 3 ft. x 2 ft. were completely isolated by cutting to the wood a channel about one inch wide. The island on the untapped tree yielded latex (a few drops) only once after opening a tapping cut on the isolated island, while that containing the original half-spiral tapping cut yielded only 20 ml. of latex initially of 30% rubber content, dropping to less than 5 ml. of latex of 10% rubber content after 12 tappings. (The yield from the same tapping cut of the latter tree before isolating the island was 270 ml.).

Comparison of Rubber from Two Tapping Cuts on a Single Tree

Common practice in slaughter-tapping is to open a second tapping cut at some distance above the existing cut, both being made full spiral, resulting in a 300% increase in tapping intensity if the frequency of tapping is maintained. This is generally found to diminish the rubber content of the latex and to result in a softer rubber but no data are available in the literature for latices collected separately from the two tapping cuts. It might be expected from the foregoing that larger areas of the upper parts of the tree would be drained as a result of the increased severity of tapping, and that the latex from these regions would appear mainly in that drawn from the upper cut so that a harder rubber would be obtained therefrom. This has been confirmed by observations (Table XI) extending over 12 weeks on five trees in which the lower half-spiral tapping cut was extended to full spiral and the newly opened upper cut, located at the top of the existing tapping panel and subsequently moved progressively upwards, was made full circumference in the form of an extended "V", thus obtaining the maximum possible isolation of the lower cut from the upper part of the tree. Tapping was twice weekly, and latices from the upper and lower cuts were bulked separately. After 12 tappings serious precoagulation

occurred in the top-cut latex and it was found necessary to introduce into the latex receptacles sufficient ammonia to give 0.1% in the total volume of latex collected; smaller doses were inadequate. No precoagulation occurred in the bottom-cut latex.

Table XI

Characteristics of latex from two tapping-cuts.

Consecutive tapping No.	Yield ml.	T.S. %	D.R.C. %	L.S.V.	Vac-dried coagulum		Mooney of smoked sheet
					D_{10} m.m.	Rec. m.m.	
SAMPLES FROM TOP CUTS							
1	660	46.6	43.3	5.0	5.1	8.3	—
3	600	37.4	33.7	5.0	4.8	7.6	108
4	1,110	36.3	33.0	—	4.6	6.3	108
5	1,100	35.4	31.8	5.2	4.76	6.74	—
8	1,070	34.3	31.0	4.7	5.43	8.30	101
10	800	33.7	—	4.9	5.48	8.34	—
12*	380	33.8	29.9	4.7	4.96	7.47	—
14	1,090	31.3	27.6	4.7	5.23	7.91	99½
16	1,210	33.8	30.0	5.1	4.5	6.5	92
18	1,250	31.0	27.2	5.5	5.0	7.2	99½
20	1,250	28.0	25.0	—	—	—	—
22	1,210	31.4	28.6	6.1	5.35	7.85	—
24	1,724	33.1	29.5	6.2	5.52	8.64	—
26	1,140	33.5	29.5	6.2	4.78	7.14	—
SAMPLES FROM BOTTOM CUTS							
1	850	45.4	41.7	4.9	5.1	8.3	—
3	1,020	39.6	35.9	5.5	4.0	4.6	86½
4	1,570	36.1	33.1	—	3.85	4.65	78
5	1,350	36.2	32.6	5.4	3.69	4.30	—
8	1,120	30.7	27.7	5.2	3.52	4.87	58½
10	1,100	32.2	—	5.3	3.78	4.35	—
12*	1,110	31.9	28.2	5.1	3.72	4.30	—
14	1,120	30.3	27.0	4.7	3.69	4.13	67
16	1,240	29.4	25.9	4.8	3.1	3.4	61½
18	1,200	28.5	25.0	5.0	3.5	3.9	65½
20	1,400	23.1	20.1	4.7	—	—	—
22	1,000	23.7	21.1	4.8	3.64	4.18	—
27	1,104	24.0	20.8	4.6	3.40	3.68	—
26	940	26.1	21.4	4.8	3.21	3.56	—

* Late tapping.

The rise in intrinsic viscosity after the 17th tapping may be due to exhaustion of available microgel from the upper part of the tree, but it is of interest that the top cut rubber does not become softer at this stage. Philpott(9) observed that harder rubbers were obtained from the bark just above the tapping panel, with a sharp difference in plasticity in passing from the renewed bark of the tapping panel to the old bark just above it.

Summary and Conclusions

Untapped or long-rested trees frequently contain microgel latex which yields solutions of low intrinsic viscosity and with only very small osmotic pressure. These latices yield very hard rubbers.

When a tree containing microgel latex is brought into tapping the inherent viscosity of solutions of its latex increases steadily, while the rubber obtained from it becomes progressively softer. After about ten tappings the latex becomes more or less normal.

Trees of clone P.B.186 do not contain much microgel latex, especially when they have once been brought into tapping and then rested. This characteristic also applies to the clonal cross P.B.186 x Tj.1.

Microgel latex appears in the crown of many trees in regular tapping, and its identification assists in defining the area of a tree not affected by tapping. There is a tendency for tapping of high yielding trees to affect the latex of a greater area of the tree than low yielders.

When two tappings cuts are opened on the same tree the latex drawn from the upper cut gives much harder rubber than that from the lower cut although the intrinsic viscosities of rubber from the two cuts are not initially different.

Acknowledgments

The author acknowledges the assistance of Dr. W. T. Chambers (B.R.P.R.A.) for the microanalyses recorded in this paper, which forms part of the programme of fundamental research undertaken by the Boards of the British Rubber Producers' Research Association and the Rubber Research Institute of Malaya.

The author particularly desires to record his appreciation of the co-operation of Mr. M. W. Philpott, Head of the Chemical Division of the Rubber Research Institute.

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